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NON-RESONANT RELATIVISTIC INTERMOLECULAR FORCES

by

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ABSTRACT

The interaction of two like atoms in degenerate quantum states of the same energy and the interaction of two unlike atoms in arbitrary states is considered in the Breit-Pauli approximation. For these non-resonant interactions the calculation of the relativistic long range interaction energy, through $O(\alpha^2)$, is discussed with specific allowance for degeneracy in the interacting atoms. Possible interactions where relativistic effects may be important are discussed. As a specific example the interaction of two spin degenerate atoms ($L=0$, $S \neq 0$) is calculated through $O(\alpha^2/R^6)$ (where R is the interatomic separation). The non-relativistic energy is given by the usual London dispersion energy which varies as $1/R^6$ while relativistic effects introduce an interaction energy which varies as α^2/R^3 .

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1. Introduction

Relativistic or retardation effects modify the interaction between atoms and molecules appreciably for large intermolecular separations, R , and in general the corresponding interaction energies for these systems cannot be calculated accurately from the Coulomb potential energy. It has been shown that moderately long range interaction energies can be calculated^{1,2} in the Breit-Pauli approximation through $\mathcal{O}(\alpha^2)$ (where $\alpha = e^2/\hbar c \sim 1/137$). By moderately long range we mean separations R sufficiently large that the charge distributions of the two interacting molecules do not overlap and yet not large enough to involve strong retardation effects, $R < \lambda$. Here $\lambda = (\alpha \Delta E)^{-1}$ is the reduced wave length characteristic of allowed transitions in the interacting molecules (ΔE is the corresponding excitation energy). For $R \sim \lambda$ or $R > \lambda$ quantum electrodynamics often must be used to calculate³ accurate interaction energies.

In this paper the interaction of two like atoms in degenerate quantum states of the same energy and the interaction of two unlike atoms in arbitrary states is considered in the Breit-Pauli approximation. For these non-resonant interactions the calculation of the relativistic interaction energy, through $\mathcal{O}(\alpha^2)$, is discussed briefly in general and allowance is made specifically for degeneracy in the interacting atoms. Then some possible interactions where relativistic effects may be important are discussed.

These interactions correspond to cases where the permanent electrostatic dipole-dipole interaction energy vanishes and the lead term in the $1/R$ -expansion of the interaction energy is given by an α^2/R^3 permanent magnetic dipole-dipole interaction energy. These magnetic interaction energies are also of importance because they do not appear to be retarded^{2,4} for very large values of R . As a specific example the interaction of two spin degenerate ($L=0, S \neq 0$) atoms is calculated through $\Theta(\alpha^2/R^3)$. It is found that the most important non-relativistic interaction energy is the usual London dispersion energy which varies as $1/R^6$ while the relativistic interaction energy contains a term which varies as α^2/R^3 . For the interaction of two non-degenerate atoms ($L = S = 0$) the results of this paper reduce to those obtained previously^{1(a)}.

In this work atomic units are used; energy $\sim e^2/a_0$, length $\sim a_0$ where a_0 is the Bohr radius. The coordinate system for the calculation of the interaction energies is the same as that used in refs. 1 and 5. For the interaction of two atoms a and b the non-relativistic eigenfunctions $\varphi_a(A)$ and $\varphi_b(B)$, respectively, represent states of sharp angular momentum (both spin S and orbital L). The set of quantum numbers A , characterizing the state of atom a is given by

$$A = (k_a, L_a, M_{L_a}, S_a, M_{S_a}) \quad (1-1)$$

where

$$L^2(a) \varphi_a(A) = L_a(L_a + 1) \varphi_a(A); \quad L_z(a) \varphi_a(A) = M_{L_a} \varphi_a(A)$$

$$S^2(a) \varphi_a(A) = S_a(S_a + 1) \varphi_a(A); \quad S_z(a) \varphi_a(A) = M_{S_a} \varphi_a(A)$$

Here $(l, k)_a$ denotes the remaining quantum numbers required for the specification of the states of the atom. The non-relativistic

Schrödinger equation for atom a is

$$H_0(a) \varphi_a(A) = E_a(k, L, S) \varphi_a(A)$$

where $H_0(a)$ is the non-relativistic Hamiltonian for the atom. In

the paper we shall often make use of the notation

$$E_a(k, L, S) = E(k_a, L_a, S_a)$$

and it should be noted that the non-relativistic energy is independent of the quantum numbers M_{L_a} and M_{S_a} .

The spin magnetic moments of the electrons in the system; H_{S1} represents the

interaction between the spin magnetic moments and the orbital

magnetic moments of the electrons in the system; H_0 is a relativistic

correction due to the variation of electron mass with velocity and

H_D appears to have no simple interpretation.

The "multipole expansion" of the Breit-Pauli Hamiltonian

is used for the calculation of long range interaction energies

through $\phi(r)$. If the charge distributions of the interacting

2. Long Range Interaction Energies in the Breit-Pauli Approximation

(a) The Multipole Expansion of the Breit-Pauli Hamiltonian

In the generalized Breit-Pauli approximation to the relativistic Hamiltonian (with nuclei held fixed)⁶ is given by⁷

$$H = H_e + \alpha^2 H_{rel} \quad (2-1)$$

where H_e is the usual non-relativistic Hamiltonian for the system. The relativistic correction, H_{rel} , includes terms which allow for magnetic interactions between the electrons in the system and has the form⁸

$$H_{rel} = H_{LL} + H_{SS} + H_{SL} + H_p + H_D \quad (2-2)$$

(1a,7)

The various terms in H_{rel} have the following significance :

H_{LL} corresponds to the interaction of the orbital magnetic moments of the electrons in the system; H_{SS} gives the interaction between the spin magnetic moments of the electrons; H_{SL} represents the interaction between the spin magnetic moments and the orbital magnetic moments of the electrons in the system; H_p is a relativistic correction due to the variation of electron mass with velocity and H_D appears to have no simple interpretation.

The "multipole expansion" of the Breit-Pauli Hamiltonian^{1(a),2,9,10,11} is used for the calculation^{1(a),2} of long range interaction energies through $\mathcal{O}(\alpha^2)$. If the charge distributions of the interacting

atoms a and b do not overlap¹² then one can show that

$$H_e = H_o(a) + H_o(b) + V_e \quad ; \quad V_e = \sum_{m=2}^{\infty} V_m / R^m \quad (2-3)$$

and

$$H_{\sigma} = H_{\sigma,0} + H_{\sigma}^{int} \quad ; \quad H_{\sigma,0} = H_{\sigma,0}(a) + H_{\sigma,0}(b)$$

$$H_{\sigma}^{int} = \sum_{m=1}^{\infty} H_{\sigma,m} / R^m \quad , \quad \sigma = LL, SS, SL, P, D. \quad (2-4)$$

In Eq. (2-3) V_e is the non-relativistic interaction potential and the expansion coefficients V_m represent the interaction⁵ of various electrostatic multipoles of atom a with those of atom b. In Eq. (2-4) the $H_{\sigma,0}(a)$ are the relativistic Hamiltonians of the isolated atom a and H_{σ}^{int} is the relativistic interaction potential corresponding to the relativistic correction σ . The expansion coefficients $H_{\sigma,m}$ represent the interaction^{1(a),9} of various orbital and spin magnetic multipoles of atom a with those of atom b. General expressions for the $H_{\sigma,m}$ are derived in ref. 9 and it should be noted that

$$H_{SL,1} = H_{SS,1} = H_{SS,2} = H_{P,m>0} = H_{D,m>0} = 0 \quad (2-5)$$

The non-zero multipole expansion coefficients, through $O(1/R^3)$, are of specific interest in this paper and are discussed briefly

in the Appendix (see also ref. 1(a)).

From semi-classical considerations^{7(c)} one would expect that two atoms a and b with magnetic dipoles $\underline{M}(a) = -\frac{\alpha}{2} [\underline{L}(a) + 2 \underline{S}(a)]$ and $\underline{M}(b) = -\frac{\alpha}{2} [\underline{L}(b) + 2 \underline{S}(b)]$ respectively, would have a magnetic dipole-dipole interaction Hamiltonian

$$H_{S.C.}^{mag} = \frac{1}{R^3} [\underline{M}(a) \cdot \underline{M}(b) - 3 M_{\frac{z}{2}}(a) M_{\frac{z}{2}}(b)] \quad (2-6)$$

The relativistic multipole expansion coefficients $H_{\sigma,3}$ for $\sigma = LL, SS$, and SL , can be written^{1(a)} in the form (see Appendix)

$$H_{\sigma,3} = \Gamma_{\sigma,3} + \chi_{\sigma,3}, \quad \chi_{SS,3} = 0 \quad (2-7)$$

where $\Gamma_{\sigma,3}$ corresponds to the semi-classical Hamiltonian and the $\chi_{\sigma,3}$ represent correction terms; thus

$$H_{S.C.}^{mag} = \frac{\alpha^2}{R^3} [\Gamma_{LL,3} + \Gamma_{SS,3} + \Gamma_{SL,3}] \quad (2-8)$$

The expansion coefficients $\Gamma_{\sigma,3}$ for $\sigma = LL, SS, SL$ represent respectively, the magnetic orbit-orbit, spin-spin and spin-orbit dipole interactions between atoms a and b.

(b) Calculation of the Interaction Energy

Consider the interaction of two atoms a and b in the quantum states A' and B' respectively. In the Breit-Pauli approximation the relativistic Schrodinger equation for the diatomic molecule $a - b$ is given by

$$H\Psi = (H_e + \alpha^2 H_{rel})\Psi = \mathcal{E}\Psi \quad (2-9)$$

This equation can be solved¹, for moderately large R , for the energy \mathcal{E} through all orders in V_e and through first order in α^2 . First the non-relativistic problem

$$H_e \Psi_K = E_K \Psi_K \quad (2-10)$$

is solved by perturbation theory using $H_0 = H_0(a) + H_0(b)$ as the unperturbed Hamiltonian and the multipole expansion of V_e as the perturbation. This gives a $1/R$ expansion for the non-relativistic wave function and energy

$$\Psi_K = \Psi_K^{(0)} + \sum_{m=3}^{\infty} \Psi_m^{(K)}/R^m \quad (2-11)$$

$$E_K = E_a(R', L', S') + E_b(R', L', S') + \sum_{m=3}^{\infty} C_m^{(K)}/R^m \quad (2-12)$$

Here K corresponds to the good quantum numbers for the combined two atom system and the $C_m(K)/R^m$ are the non-relativistic interaction energies which include⁵ dispersion forces as well as terms representing the direct interaction between permanent electrostatic multipole moments of the interacting atoms. The zero-th order wave functions, $\psi_K^{(0)}$, must be chosen to diagonalize¹³ appropriate perturbation Hamiltonians (see below). Having obtained an expression for the non-relativistic wave function it is easy to show^{1(a)} that one can obtain a $1/R$ expansion¹⁴ for the energy E through $\Theta(\alpha^2)$

$$E_K = E_K + \alpha^2 \sum_{\sigma} E_{\sigma}^{(1)}(K) \quad (2-13)$$

where

$$E_{\sigma}^{(1)}(K) = E_{\sigma,0}^{(1)(a)} + E_{\sigma,0}^{(1)(b)} + \sum_{m=1}^{\infty} W_{\sigma,m}(K)/R^m \quad (2-14)$$

and

$$W_{\sigma,m}(K) = \sum_{l=0}^m \sum_{q=0}^{m-l} \langle \psi_q(K) | H_{\sigma,l} | \psi_{m-l-q}(K) \rangle. \quad (2-15)$$

Here the $E_{\sigma,0}^{(1)(a)}$ are the relativistic corrections to the energy of the isolated atom and the $W_{\sigma,m}(K)/R^m$ are the $\Theta(\alpha^2)$ relativistic interaction energies.

Combining the above results the interaction energy (including

both relativistic and non-relativistic terms) is given by

$$\mathcal{E}_{ab}(K) = \sum_{m=3}^{\infty} C_m(K)/R^m + \sum_{\sigma} \mathcal{E}_{ab}^K(\sigma) \quad (2-16)$$

where

$$\mathcal{E}_{ab}^K(\sigma) = \alpha^2 \sum_{m=1}^{\infty} W_{\sigma,m}(K)/R^m \quad (2-17)$$

$\mathcal{E}_{ab}^K(\sigma)$ is the relativistic interaction energy arising from the interaction of magnetic multipoles which occur in the multipole expansion of H_{σ}^{int} . The lead terms in the expansion of $\mathcal{E}_{ab}(K)$ arise from coefficients $C_m(K)$ that are first order in V_e and zero-th order in α^2 or from coefficients $W_{\sigma,m}(K)$ that are first order in α^2 and zero-th order in V_e . It is easy to show that the interaction energy through $\mathcal{O}(\alpha^2/R^3)$ is given by¹⁵

$$\mathcal{E}_{ab}(K) = \frac{C_3(K)}{R^3} + \alpha^2 \left[\frac{W_{LL,1}(K)}{R} + \frac{W_2(K)}{R^2} + \frac{W_3(K)}{R^3} \right] + \dots \quad (2-18)$$

where

$$C_3(K) = \langle \psi_K^{(0)} | V_3 | \psi_K^{(0)} \rangle \quad (2-19)$$

$$W_2(K) = W_{LL,2}(K) + W_{SL,2}(K) \quad (2-20)$$

$$W_3(K) = W_{LL,3}(K) + W_{SL,3}(K) + W_{SS,3}(K) \quad (2-21)$$

and

$$W_{\sigma,m}(K) = \langle \psi_K^{(0)} | H_{\sigma,m} | \psi_K^{(0)} \rangle, \quad m = 1, 2, 3. \quad (2-22)$$

The coefficients $C_m(K)$ and $W_{\sigma,m}(K)$, for $m \geq 3$ involve¹⁶ the $\psi_m(K)$ with values of $m \geq 3$. For the interaction of two non-degenerate ($L'=S'=0$) atoms it is easy to show that the interaction energy through $O(\lambda^2/R^3)$ is zero. In this case the interaction energy has the form¹

$$E_{ab} = C_6/R^6 + \lambda^2 W_{LL,4}/R^4 + \lambda^2 W_6/R^6 + \dots \quad (2-23)$$

and this result has been discussed in detail in ref. 1.

The limitations on the use of the Breit-Pauli approximation are discussed in detail¹⁷ in refs. 1 and 7. Of particular importance is the fact that in general the interaction energies calculated using this approximation are accurate only for $R < \lambda$. For example¹ for the interaction of non-degenerate atoms the Breit-Pauli approximation fails to represent the interaction accurately for $R > 0.6\lambda$. It should be noted however that in the non-resonant

interactions discussed here the energy corresponding to the interaction of permanent electrostatic or magnetic dipoles appears to be valid^{2,4} even for large R .

Construction of the Zero-th Order Wavefunctions

In order to actually calculate the interaction energy for a specific problem one must know the zero-th order wave functions $\psi_K^{(0)}$. These are constructed from the solutions to the non-relativistic Schrodinger equation for the isolated atoms a and b in the quantum states A' and B' respectively. Here we will limit the discussion to non-resonant interactions.

Instead of using eigenfunctions of $L_z(a)$ and $S_z(a)$ to construct the $\psi_K^{(0)}$, it will often be more convenient¹⁸ for our purposes to choose instead orthonormal eigenfunctions of $J^2(a)$ and $J_z(a)$ where $\underline{J}(a) = \underline{L}(a) + \underline{S}(a)$;

$$\varphi_a(R', J', M_J') = \sum_{M_L', M_S'} \langle \varphi_a(A') | \varphi_a(R', J', M_J') \rangle \varphi_a(A'). \quad (2-24)$$

Here $J'_a = L'_a + S'_a, \dots, |L'_a - S'_a|$ and where, from Eq. (1-3),

$$H_0(a) \varphi_a(R', J', M_J') = E_a(R', L', S') \varphi_a(R', J', M_J'). \quad (2-25)$$

The proper non-relativistic zero-th order wave functions, $\Psi_K^{(0)}$, for the long range interaction of two like atoms in states with the same energy or two unlike atoms in arbitrary states (non-resonant interactions) can be written in the following form¹⁹

$$\Psi_K^{(0)} = \sum_{J_a, J_b} \sum_{M_a, M_b} \langle \varphi_a(R', J', M_J) \varphi_b(R', J', M_J) | \Psi_K^{(0)} \rangle \times \varphi_a(R', J', M_J) \varphi_b(R', J', M_J) \quad (2-26)$$

where of course $H_0 \Psi_K^{(0)} = [E_a(R', L', S') + E_b(R', L', S')] \Psi_K^{(0)}$.

The coefficients $\langle \varphi_a(R', J', M_J) \varphi_b(R', J', M_J) | \Psi_K^{(0)} \rangle$ are chosen to diagonalize¹³ appropriate perturbation Hamiltonians (i.e., the desired V_m and $H_{\sigma, m}$) subject to the condition that

$$\langle \Psi_K^{(0)} | \Psi_{K'}^{(0)} \rangle = \delta_{K, K'}. \quad (2-27)$$

3. Non-resonant Interaction Energies for Atoms in Degenerate States

In this section we prove two theorems that apply for non-resonant atomic interactions.

Let the two interacting atoms a and b have electrostatic dipole moments $\underline{\mu}(a)$ and $\underline{\mu}(b)$ and magnetic dipole moments $\underline{M}(a)$ and $\underline{M}(b)$ respectively. Then from semi-classical considerations one would expect that the interaction energy through $O(\alpha^2/R^3)$ would be given by

$$E_{s.c.}(K) = C_2(K)/R^3 + \alpha^2 W_{3, s.c.}(K)/R^3 + \dots \quad (3-1)$$

where

$$W_{3,s.c.}(K) = \langle \Psi_K^{(0)} | \Gamma_{LL,3} + \Gamma_{SS,3} + \Gamma_{SL,3} | \Psi_K^{(0)} \rangle \quad (3-2)$$

Here $C_3(K)/R^3$ is the usual permanent electrostatic dipole-dipole interaction energy and $\alpha^2 W_{3,s.c.}(K)/R^3$ is the permanent magnetic dipole-dipole interaction²⁰ energy that one would expect from Eq. (2-8). Using Eq. (3-1) and (2-18) the interaction energy through $O(\alpha^2/R^3)$ can be written as

$$E_{ab}(K) = E_{s.c.}(K) + E_{n.c.}(K) + \dots \quad (3-3)$$

where

$$E_{n.c.}(K) = \alpha^2 [W_{LL,1}(K)/R + W_2(K)/R^2 + W_{3,n.c.}(K)/R^3] \quad (3-4)$$

$$W_{3,n.c.}(K) = \langle \Psi_K^{(0)} | \chi_{LL,3} + \chi_{SL,3} | \Psi_K^{(0)} \rangle \quad (3-5)$$

The interaction energy $E_{n.c.}(K)$ is a non-classical correction to the semi-classical result of Eq. (3-1).

Theorem I: The interaction energy through $O(\alpha^2/R^3)$ is identically equal to the semi-classical result,

$$E_{ab}(K) = E_{s.c.}(K) \quad (3-6)$$

Proof: Define the integrals

$$\begin{aligned} I_1(a) &= \langle \varphi_a(k', J', M_J') | J_1^m(a) | \varphi_a(k', J, M_J) \rangle \\ I_2(a) &= \langle \varphi_a(k', J', M_J') | D_2^m(a) | \varphi_a(k', J, M_J) \rangle \\ I_3(a) &= \langle \varphi_a(k', J', M_J') | O_1^m(a) | \varphi_a(k', J, M_J) \rangle \end{aligned} \quad (3-7)$$

where J'_a and J_a can have the values $|L'_a + S'_a|, \dots, |L'_a - S'_a|$ and similarly for atom b . The spherical tensor operators J_1^m , D_2^m and O_1^m are discussed in the Appendix. Using the commutator relations given by Eqs. (A-2) - (A-4) it is easy to show that²¹

$$I_1(a) = I_2(a) = I_3(a) = 0 \quad (3-8)$$

and similarly for atom b .

From Eqs. (2-19)-(2-21) and (2-26) and the expressions for the multipole expansion coefficients given in the Appendix one can show that the coefficients $W_{LL,1}(K)$, $W_2(K)$ and $W_{3,N.C.}(K)$ are expressible as a sum of terms each of which contains at least one of the integrals given by Eq. (3-8). Hence $\mathcal{E}_{N.C.}(K)$ vanishes and one obtains the result of Eq. (3-6).

We conclude from theorem I that although the relativistic Hamiltonian's H_{LL} and H_{SL} yield multipole expansion coefficients of $\mathcal{O}(\alpha^2/R)$ and $\mathcal{O}(\alpha^2/R^2)$, there are no relativistic interaction energies of the same order in $1/R$.

From Eqs. (3-1) and (3-6) it is clear that for the relativistic interaction energies to be important the non-relativistic interaction energy $C_3(\kappa)/R^3$ must vanish leaving

$$E_{ab}(\kappa) = \alpha^2 W_{S.E.}(\kappa)/R^3 + \dots \quad (3-9)$$

In Sec. 4 various possible interactions are discussed which lead to an interaction energy of the form given by Eq. (3-9) and the case of the spin-degenerate ($L'_a = L'_b = 0, S'_a \neq 0, S'_b \neq 0$) interaction is worked out explicitly through $O(\alpha^2/R^6)$.

Theorem II: The interaction energies that are first order in V_e and zero-th order in α^2 or first order in α^2 and zero-th order in V_e are identically zero when averaged over the original zero-th order degenerate states²².

Proof: The interaction energies of interest in the theorem involve matrix elements of the type

$$\langle T \rangle_{\kappa} = \langle \Psi_{\kappa}^{(0)} | T | \Psi_{\kappa}^{(0)} \rangle \quad (3-10)$$

where T is a perturbation operator which can be written symbolically^{1(a),9} (see Appendix) by

$$T = \sum_{l_1 \neq 0} \sum_{l_2 \neq 0} \sum_m \Delta(l_1, l_2, m) T_{l_1}^{-m}(a) T_{l_2}^m(b). \quad (3-11)$$

Here the $T_{\ell}^m(a)$ are irreducible spherical tensor operators²³ with respect to the total angular momentum operator, $\underline{J}(a)$, of atom a and similarly for atom b , while $\Delta(l_1, l_2, m)$ is a number.

Summing $\langle T \rangle_K$ over all the zero-th order degenerate states and using Eqs. (2-26) and (3-10) gives

$$\begin{aligned} \langle \bar{T} \rangle_K = \sum_K \langle T \rangle_K &= \sum_{J_a, J_b} \sum_{M_{J_a}, M_{J_b}} \sum_{l_1, l_2, m} \Delta(l_1, l_2, m) \\ &\times \langle \varphi_a(k', J', M_{J'}) | T_{\ell_1}^{-m}(a) | \varphi_a(k', J', M_{J'}) \rangle \\ &\times \langle \varphi_b(k', J', M_{J'}) | T_{\ell_2}^m(b) | \varphi_b(k', J', M_{J'}) \rangle. \end{aligned} \quad (3-12)$$

This expression can be simplified by using the Wigner-Eckart theorem^{23,24} and introducing the Clebsch-Gordan coefficient C ,

$$\begin{aligned} \langle \varphi_a(k', J', M_{J'}) | T_{\ell_1}^{-m}(a) | \varphi_a(k, J, M_J) \rangle \\ = C(J_a, l_1, J_a'; M_{J_a}, -m, M_{J_a}') \\ \times \langle k_a', J_a' || T_{\ell_1}(a) || k_a, J_a \rangle \end{aligned} \quad (3-13)$$

where $\langle k_a', J_a' || T_{\ell_1}(a) || k_a, J_a \rangle$ is the reduced matrix element^{23,24} for the set of tensors $T_{\ell_1}^{-m}(a)$ and similarly for atom b .

Applying the Wigner Eckart theorem to Eq. (3-12) and using the

orthogonality condition $\sum_{M'_J} C(J'l, J'; M'_J, 0, M'_J) = \delta_{l,0}$
 it is easy to show that $\langle T \rangle_K = 0$ and hence theorem II.

As a result of theorem II when the interaction energy is averaged over all original degeneracies the relativistic interaction energy through $O(\alpha^2)$ will have a lead term given by the $O(\alpha^2/R^4)$ energy discussed previously¹ and the non-relativistic interaction energy will have a lead term given by the London dispersion energy (see Sec. 4 for an example).

4. Examples

For the interaction of degenerate atoms the lead term in the $1/R$ -expansion of the non-relativistic interaction energy is usually the $1/R^5$ electrostatic quadrupole-quadrupole energy. However, in some cases, the non-relativistic interaction energy can have lower order terms in $1/R$. For example for the interaction of two hydrogen atoms, in states with principle quantum number $n=2$, the interaction energy has an $1/R^3$ electrostatic dipole-dipole term (see ref. 12 and footnote 21). In general, then, if the non-relativistic interaction energy $C_2(K)/R^3$ vanishes there is a possibility that the relativistic corrections $\alpha^2 W_{3,s.c.}(K)/R^3$ may be important. For L'_a or L'_b equal zero $C_2(K)$ vanishes and from the selection rules²³ for the relativistic multipole expansion coefficients $\Gamma_{LL,3}$, $\Gamma_{SS,3}$ and $\Gamma_{SL,3}$ one can select interactions for which the relativistic interaction energies of $O(\alpha^2/R^3)$ are not zero. Some possible interactions are given in Table I [note $\langle \psi_K^{(0)} | \Gamma_{LL,3} | \psi_K^{(0)} \rangle = 0$ if L_a or L_b equal zero].

Table I

Some Possible Interactions for which $C_2(K) = 0$ and

$$W_{3,S.C.} = \langle \Psi_K^{(0)} | \Gamma_{SS,3} + \Gamma_{SL,3} | \Psi_K^{(0)} \rangle \neq 0$$

L_a	L_b	S_a	S_b	$\langle \Psi_K^{(0)} \Gamma_{SS,3} \Psi_K^{(0)} \rangle$	$\langle \Psi_K^{(0)} \Gamma_{SL,3} \Psi_K^{(0)} \rangle$
0	0	$\neq 0$	$\neq 0$	$\neq 0$	0
$\neq 0$	0	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$
0	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$
$\neq 0$	0	0	$\neq 0$	0	$\neq 0$
0	$\neq 0$	$\neq 0$	0	0	$\neq 0$

The Interaction of Two Spin Degenerate Atoms

As a specific example consider the interaction of two atoms a and b in the states A' and B' defined by

$$A' = (R_a', 0, 0, S_a', M_{S_a}')$$

$$B' = (R_b', 0, 0, S_b', M_{S_b}')$$

In this section the interaction energy for this problem, $E_{ab}(K)$ is calculated through $O(\alpha^2/R^6)$. The mathematical techniques used, which include applications of the Wigner-Eckart theorem, have been discussed in detail previously^{1(a),26} and will be mentioned here only briefly.

The non-relativistic zero-th order wave functions have the form²⁷

$$\Psi_K^{(0)} = \sum_{M'_a, M'_b} \langle \varphi_a(A') \varphi_b(B') | \Psi_K^{(0)} \rangle \varphi_a(A') \varphi_b(B') \quad (4-2)$$

where

$$\begin{aligned} \langle \Psi_K^{(0)} | \Psi_{K'}^{(0)} \rangle &= \sum_{M'_a, M'_b} \langle \varphi_a(A') \varphi_b(B') | \Psi_{K'}^{(0)} \rangle \langle \Psi_K^{(0)} | \varphi_a(A') \varphi_b(B') \rangle \\ &= \delta_{K, K'} \end{aligned} \quad (4-3)$$

Since the degeneracy in the problem is characterized by the spin projection quantum numbers of the interacting atoms it cannot be removed by the spin free perturbations V_e , H_{LL} , H_p and H_D . Also these spin free perturbations are diagonal with respect to the $\Psi_K^{(0)}$ for any choice of the expansion coefficients $\langle \varphi_a(A') \varphi_b(B') | \Psi_K^{(0)} \rangle$ consistent with Eq. (4-3). Using Eq. (4-3) it is easy to show that the spin free interaction energies $C_m(K)/R^m$ and $\alpha^2 W_{\sigma, m}(K)/R^m$, for $\sigma = LL, p$, and D , are independent of the quantum number K and for convenience we write

$$C_m(K) = C_m ; W_{\sigma, m}(K) = W_{\sigma, m} , \sigma = LL, p, D. \quad (4-4)$$

Through $O(1/R^6)$ the non-relativistic interaction energy is given by the London²⁸ dispersion energy C_6/R^6 where

$$C_6 = -\frac{3}{2} \sum_{k_a, k_b} \frac{f^{(a)}(k_a, l, S') f^{(b)}(k_b, l, S')}{[\Delta E_a(k_a, l, S') + \Delta E_b(k_b, l, S')] \Delta E_a(k_a, l, S') \Delta E_b(k_b, l, S')} \quad (4-5)$$

Here $f^{(a)}(k, l, S')$ is the mean oscillator strength for the transition $(k'_a, L_a=0, S'_a) \rightarrow (k_a, L_a=1, S'_a)$;

$$f^{(a)}(k, l, S') = 2 \Delta E_a(k, l, S') |\langle \psi_a(k', 0, 0, S', M'_S) | \mu_z(a) | \psi_a(k, 1, 0, S', M'_S) \rangle|^2 \quad (4-6)$$

where $\Delta E_a(k, l, S') = E_a(k, l, S') - E_a(k, 0, S')$

is the excitation energy corresponding to this transition. The integrals in Eq. (4-6) are independent of the choice of M'_S and $-S' \leq M'_S \leq S'$. Unless the states labeled by the quantum numbers A' and B' happen to correspond to degenerate ground states the coefficient C_6 is not necessarily negative and the London dispersion energy is not necessarily attractive.

The only non-zero contributions to the interaction energy, through $O(\alpha^2/R^6)$, from the spin free relativistic Hamiltonians are given by

$$E_{ab}(LL) = \alpha^2 W_{LL,4} / R^4 + \alpha^2 W_{LL,6} / R^6 \quad (4-7)$$

and

$$E_{ab}(\sigma) = \alpha^2 W_{\sigma,6} / R^6, \quad \sigma = P, D. \quad (4-8)$$

The most important contribution from H_{LL} , H_P and H_D to the interaction energy is given by $\alpha^2 W_{LL,4} / R^4$ where^{1,29}

$$\begin{aligned}
 W_{LL,4} &= 2 \langle \psi_3(k) | H_{LL,1} | \psi_K^{(0)} \rangle \\
 &= \frac{1}{2} \sum_{k_a, k_b} \frac{f^{(a)}(k, l, s') f^{(b)}(k, l, s')}{[\Delta E_a(k, l, s') + \Delta E_b(k, l, s')]}
 \end{aligned}
 \tag{4-9}$$

For the interaction of two ground state atoms $W_{LL,4}$ is positive giving rise to a repulsive interaction energy. This is not necessarily the case for an interaction involving a degenerate atom. The coefficients corresponding to the $O(\alpha^2/R^6)$ interaction energies in Eqs. (4-7) and (4-8) are given by

$$\begin{aligned}
 W_{LL,6} &= 2 \langle \psi_K^{(0)} | H_{LL,2} | \psi_4(k) \rangle + 2 \langle \psi_K^{(0)} | H_{LL,3} | \psi_3(k) \rangle \\
 &\quad + 2 \langle \psi_K^{(0)} | H_{LL,0} | \psi_6(k) \rangle + \langle \psi_3(k) | H_{\sigma,0} | \psi_3(k) \rangle
 \end{aligned}
 \tag{4-10}$$

$$\begin{aligned}
 W_{\sigma,6} &= 2 \langle \psi_K^{(0)} | H_{\sigma,0} | \psi_6(k) \rangle + \langle \psi_3(k) | H_{\sigma,0} | \psi_3(k) \rangle. \\
 &\quad \sigma = p, D
 \end{aligned}
 \tag{4-11}$$

The explicit expressions for the coefficients given by Eqs. (4-10) and (4-11) are essentially identical to those for the interaction of two non-degenerate atoms^{1(a)} and since they give rise to interaction energies of $O(\alpha^2)$ smaller than the London energy we do not consider them further here.

It can be shown by straightforward, but lengthy, calculation involving the Wigner-Eckart theorem that the spin orbit Hamiltonian, H_{SL} , makes no contribution to the interaction energy through $O(\alpha^2/R^6)$.

The spin-spin Hamiltonian is not diagonal with respect to the non-relativistic zero-th order wave functions, $\psi_K^{(0)}$, for arbitrary choices of the expansion coefficients $\langle \varphi_a(A') \varphi_b(B') | \psi_K^{(0)} \rangle$. These coefficients are chosen to satisfy Eq. (4-3) and to diagonalize the (spin-dipole)-(spin-dipole) interaction Hamiltonian;

$$\langle \psi_K^{(0)} | H_{SS,3} | \psi_{K'}^{(0)} \rangle = W_{SS,3}(K) \delta_{K,K'}. \quad (4-12)$$

It can be shown that the zero-th order wave functions calculated in this manner ensure that the spin-spin Hamiltonian, H_{SS} , is diagonal with respect to the $\psi_K^{(0)}$ (at least through $O(\alpha^2/R^6)$). It should be pointed out that the diagonalization of $H_{SS,3}$ can be carried out exactly since $H_{SS,3}$ is expressed in terms of irreducible spherical spin tensors, S_1^m , of the atoms a and b . The required integrals over these spin tensors can be calculated exactly²³;

$$\begin{aligned} & \langle \varphi_a(k', L', M_L', S', M_S') | S_1^m | \varphi_a(k, L, M_L, S, M_S) \rangle \\ &= \delta_{k',k} \delta_{L',L} \delta_{M_L',M_L} \delta_{S',S} [S(S+1)]^{1/2} \\ & \quad \times C(S, S'; M_S, m, M_S'). \end{aligned}$$

(4-13)

Substituting Eqs. (4-2), (A-5) into Eq. (4-12) and using Eq. (4-13)

one obtains

$$\begin{aligned}
 W_{SS,3}(K) = & \sum_{M'_a, M'_b} \sum_{m=-1}^1 \beta_{SS,3}^{(m)} \langle \varphi_a(k', 0, 0, S', M'_a) \varphi_b(k', 0, 0, S', M'_b) | \psi_K^{(0)} \rangle \\
 & \times \langle \psi_K^{(0)} | \varphi_a(k', 0, 0, S', M'_a - m) \varphi_b(k', 0, 0, S', M'_b + m) \rangle \\
 & \times C(S'_a, 1, S'_a; M'_a, -m) C(S'_b, 1, S'_b; M'_b, m).
 \end{aligned}
 \tag{4-14}$$

In general $W_{SS,3}(K)$ is non-zero and gives rise to a relativistic (spin-dipole)-(spin-dipole) interaction energy $\alpha^2 W_{SS,3}(K)/R^3$.

The contribution of H_{SS} to the interaction energy through $O(\alpha^2/R^6)$ is given by

$$\mathcal{E}_{ab}^K(SS) = \alpha^2 W_{SS,3}(K)/R^3 + \alpha^2 W_{SS,6}(K)/R^6
 \tag{4-15}$$

where

$$W_{SS,6}(K) = 2 \langle \psi_K^{(0)} | H_{SS,0} | \psi_b(K) \rangle + \langle \psi_b(K) | H_{SS,0} | \psi_b(K) \rangle.
 \tag{4-16}$$

The coefficient $W_{SS,6}$ is similar in structure to the result for the interaction of two non-degenerate atoms^{1(a)} and since it is of $O(\alpha^2)$ smaller than the London dispersion energy we do not consider it further here.

Combining the results of Eqs. (4-5)-(4-15) we obtain an expression for the interaction energy for the spin degenerate problem

$$E_{ab}(K) = \frac{C_6}{R^6} + \alpha^2 \frac{W_{SS,3}(K)}{R^3} + \alpha^2 \frac{W_{LL,4}}{R^4} + \alpha^2 \frac{W_6}{R^6} + \dots$$

(4-15)

Here $W_6 = \sum_{\ell} W_{\ell,6}$ and since the $\Theta(\alpha^2/R^6)$ energy is of order 5×10^{-5} smaller than the London energy we shall neglect³⁰ it in what follows.

In order to obtain numerical values for the coefficients in Eq. (4-15) consider the interaction of two doublet atoms ($S'_a = S'_b = \frac{1}{2}$). The proper zero-th order wave functions which diagonalize $H_{SS,3}$ and the corresponding coefficients $W_{SS,3}(K)$ are given by³¹

$$\begin{aligned} \Psi^{(0)}(^1\Sigma_0) &= \frac{1}{\sqrt{2}} [\varphi_a(1,0,0,1/2,-1/2) \varphi_b(1,0,0,1/2,1/2) - \varphi_a(1,0,0,1/2,1/2) \varphi_b(1,0,0,1/2,-1/2)] \\ \Psi^{(0)}(^3\Sigma_1) &= \varphi_a(1,0,0,1/2,1/2) \varphi_b(1,0,0,1/2,1/2) \\ \Psi^{(0)}(^3\Sigma_0) &= \frac{1}{\sqrt{2}} [\varphi_a(1,0,0,1/2,-1/2) \varphi_b(1,0,0,1/2,1/2) + \varphi_a(1,0,0,1/2,1/2) \varphi_b(1,0,0,1/2,-1/2)] \\ \Psi^{(0)}(^3\Sigma_{-1}) &= \varphi_a(1,0,0,1/2,-1/2) \varphi_b(1,0,0,1/2,-1/2) \end{aligned}$$

(4-16)

$$W_{SS,3}(^1\Sigma_0) = 0, \quad W_{SS,3}(^3\Sigma_0) = +1$$

$$W_{SS,3}(^3\Sigma_1) = W_{SS,3}(^3\Sigma_{-1}) = -1/2$$

(4-17)

The vanishing of the coefficient $W_{SS,3} (^1\Sigma_0)$ corresponds to the fact that the $^1\Sigma_0$ state of the hydrogen molecule has zero total spin. To calculate values for the other coefficients in Eq. (4-15) explicit expressions for the wave functions of the interacting atoms are required. These coefficients are readily available³² or estimated³³ for the interaction of two ground state hydrogen atoms. The resulting interaction energies are

$$\begin{aligned} \mathcal{E}_{ab} (^1\Sigma_0) &= -\frac{6.50}{R^6} + \frac{0.40\alpha^2}{R^4} + \dots \\ \mathcal{E}_{ab} (^3\Sigma_0) &= -\frac{6.50}{R^6} + \frac{0.40\alpha^2}{R^4} + \frac{\alpha^2}{R^3} + \dots \\ \mathcal{E}_{ab} (^3\Sigma_1) = \mathcal{E}_{ab} (^3\Sigma_{-1}) &= -\frac{6.50}{R^6} + \frac{0.40\alpha^2}{R^4} - \frac{\alpha^2}{2R^3} + \dots \end{aligned} \quad (4-18)$$

The relativistic interaction energies given in Eqs. (4-18) are compared with the London dispersion energy, $U_6 = -6.50/R^6$ in Fig. I where ratios of the form $\mathcal{E}_{ab}(R)/U_6$ are plotted against the interatomic separation R . For the interactions represented by the $^3\Sigma$ potential energy curves the relativistic interaction energy, which is dominated by the (spin-dipole)-(spin-dipole) energy, is an appreciable fraction of the London dispersion energy for relatively³⁴ small values of R . For example for the $^3\Sigma_0$ curve

the relativistic interaction energy is 10 per cent of the London energy at $R \sim 22a_0$ while for the $^3\Sigma_{+1}$ states the relativistic energies are 10 per cent of the London energy for $R \sim 30a_0$. When the sum of the three $^3\Sigma$ potential energy curves is taken the (spin-dipole)-(spin-dipole) interaction energy vanishes in agreement with Theorem II.

The relativistic interaction energies of $O(1/R^3)$ discussed in this paper may be of importance in atomic scattering experiments³⁵. They are also important because they appear not to be retarded^{2,4} at large intermolecular separations and therefore will sometimes⁴ be the lead term in the $1/R$ expansion of the very long range interaction energy.

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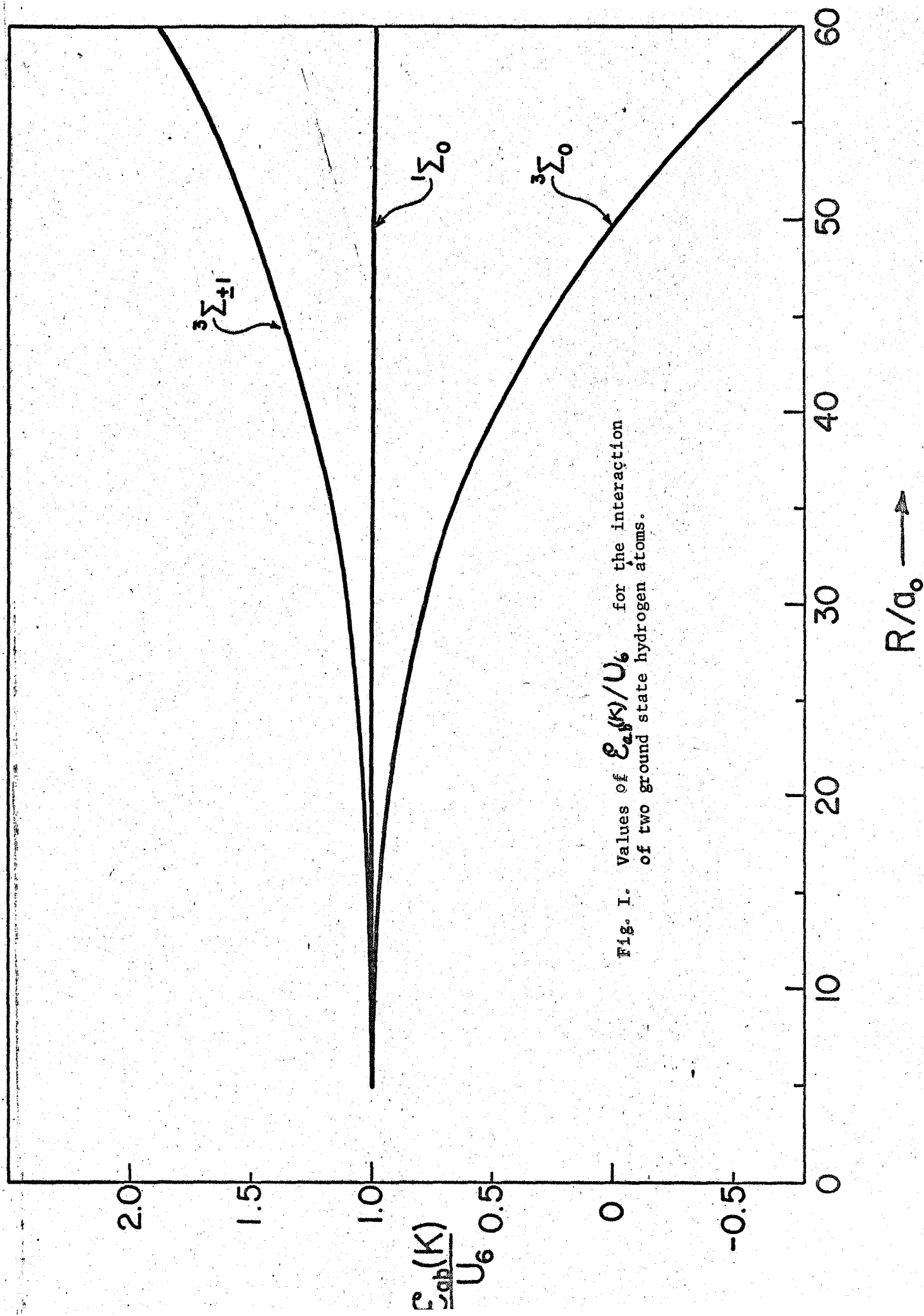


Fig. 1. Values of $E_{ab}(K)/U_6$ for the interaction of two ground state hydrogen atoms.

Appendix. Expansion Coefficients of the Breit-Pauli Hamiltonian

In this Appendix we give explicit expressions for the expansion coefficients $H_{LL,m}$, $H_{SS,m}$, $H_{SL,m}$ and V_m , for $0 < m < 4$, that are required in Secs. 3 and 4. These are also given in ref. 1(a) but appear here in a much simplified form. The multipole expansion coefficients are expressed as products of irreducible spherical tensor operators of the atoms a and b . Most of these operators (see below) are defined in ref. 1(a). In what follows the space and spin coordinates of an electron in atom a , referred to the nucleus of atom a , are designated by \underline{r}_A and \underline{s}_A respectively. We also make use of a permutation operator P_{ab} which permutes all indices associated with atom a with the corresponding indices of atom b ; $P_{ab} f(a,b) = f(b,a)$.

It is convenient to define the following tensorial operators;

$$\begin{aligned} O_1^m(a) &= \sum_A T_1^m(\underline{p}_A \underline{s}_A) \quad , \quad N_1^m(a) = \sum_A T_1^m(\underline{r}_A \underline{s}_A) \\ K_2^m(a) &= \sum_A T_2^m(\underline{r}_A \underline{s}_A) \end{aligned} \quad (A-1)$$

and similarly for atom b . The tensors $T_1^m(\underline{AB})$, $T_2^m(\underline{AB})$, and the other spherical tensors used in this paper are defined in ref. 1(a). The following commutation relations for some of the tensorial operators are useful

$$i [H_0(a), R_1^m(a)] = J_1^m(a) \quad (A-2)$$

$$i/2 [H_0(a), Q_2^m(a)] = D_2^m(a) \quad (A-3)$$

$$i [H_0(a), N_1^m(a)] = O_1^m(a) \quad (A-4)$$

Non-zero Multipole Expansion Coefficients through $O(1/R^3)$

$$V_3 = \sum_{m=-1}^1 \beta_e^{(m)} R_1^{-m}(a) R_1^m(b) \quad ; \quad \beta_e(0) = -2, \quad \beta_e(\pm 1) = -1$$

$$H_{LL,1} = \sum_{m=-1}^1 \beta_{LL,1}^{(m)} J_1^{-m}(a) J_1^m(b) \quad ; \quad \beta_{LL,1}(0) = -1, \quad \beta_{LL,1}(\pm 1) = 1/2$$

$$H_{LL,2} = \{1 - P_{ab}\} \left\{ \sum_{m=\pm 1} \beta_{LL,2}^{(m)} [L_1^{-m}(a) J_1^m(b) - (3/2)^{1/2} D_2^0(a) J_1^0(b)] \right\}$$

$$\beta_{LL,2}(-1) = -\beta_{LL,2}(1) = -i/2$$

$$H_{SL,2} = \{1 - P_{ab}\} \sum_{m=\pm 1} \beta_{SL,2}^{(m)} J_1^{-m}(a) S_1^m(b)$$

$$\beta_{SL,2}(-1) = -\beta_{SL,2}(1) = -i$$

$$\Gamma_{LL,3} = \sum_{m=-1}^1 \beta_{LL,3}^{(m)} L_1^{-m}(a) L_1^m(b)$$

$$\beta_{LL,3}(0) = -1/2, \quad \beta_{LL,3}(\pm 1) = -1/4$$

$$\chi_{LL,3} = \{1 + \rho_{ab}\} \left\{ \sum_{m=\pm 1} \gamma_{LL,3}^{(m)} D_2^{-m}(a) L_1^m(b) + \sum_{m=0,1} \eta_{LL,3}^{(m)} D_2^{-m}(a) D_2^m(b) \right. \\ \left. + \sum_{m=-1}^1 \left[\mathcal{H}_{LL,3}^{(m)} \gamma_1^{-m}(a) + \lambda_{LL,3}^{(m)} \gamma_2^{-m}(a) + \mu_{LL,3}^{(m)} \gamma_3^{-m}(a) \right] \mathcal{J}_1^m(b) \right\}$$

$$\gamma_{LL,3}^{(-1)} = -\gamma_{LL,3}^{(+1)} = -\frac{3i}{2\sqrt{2}} ; \eta_{LL,3}^{(+1)} = \eta_{LL,3}^{(0)} = \frac{3}{2} ; \mathcal{H}_{LL,3}^{(0)} = \frac{1}{\sqrt{15}} , \mathcal{H}_{LL,3}^{(\pm 1)} = \frac{1}{2\sqrt{15}}$$

$$\lambda_{LL,3}^{(0)} = 0 ; \lambda_{LL,3}^{(-1)} = -\lambda_{LL,3}^{(+1)} = -\frac{\sqrt{3}}{2} ; \mu_{LL,3}^{(0)} = -3\left(\frac{2}{5}\right)^{1/2} , \mu_{LL,3}^{(\pm 1)} = -\frac{3}{2\sqrt{15}}$$

$$\Gamma_{SL,3} = \{1 + \rho_{ab}\} \sum_{m=-1}^1 \beta_{SL,3}^{(m)} L_1^{-m}(a) S_1^m(b) ; \beta_{SL,3}^{(0)} = -1 , \beta_{SL,3}^{(\pm 1)} = -1/2$$

$$\chi_{SL,3} = \{1 + \rho_{ab}\} \left\{ \sum_{m=\pm 1} \delta_{SL,3}^{(m)} D_2^{-m}(a) S_1^m(b) + \sum_{m=-1}^1 \eta_{SL,3}^{(m)} R_1^{-m}(a) O_1^m(b) \right. \\ \left. + \sum_{m=-1}^1 \mathcal{J}_1^{-m}(a) \left[\gamma_{SL,3}^{(m)} N_1^m(b) + \mathcal{H}_{SL,3}^{(m)} K_2^m(b) \right] \right\}$$

$$\delta_{SL,3}^{(-1)} = -\delta_{SL,3}^{(+1)} = -\frac{3i}{\sqrt{2}} ; \eta_{SL,3}^{(0)} = i\sqrt{2} , \eta_{SL,3}^{(\pm 1)} = \frac{i}{\sqrt{2}}$$

$$\mathcal{H}_{SL,3}^{(0)} = 0 , \mathcal{H}_{SL,3}^{(-1)} = -\mathcal{H}_{SL,3}^{(+1)} = \frac{3i}{\sqrt{2}}$$

$$\Gamma_{SS,3} = \sum_{m=-1}^1 \beta_{SS,3}^{(m)} S_1^{-m}(a) S_1^m(b) ; \beta_{SS,3}^{(0)} = -2 , \beta_{SS,3}^{(\pm 1)} = -1$$

(A-5)

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individual problem must be considered separately. In some
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successive diagonalization of various perturbation Hamiltonians.
Other problems may require simultaneous diagonalization of the
perturbation Hamiltonians and the resulting zero-th order wave

functions can depend on $1/R$. The order (in α^2 or $1/R$) of the dominant terms in the interaction energy will be unaffected by the terms in the zero-th order wave function that vary as $1/R$ and for convenience we will assume that the $\psi_K^{(0)}$ are independent of $1/R$. For discussions on some of these points see for example J. K. Knipp, Phys. Rev. 53, 734 (1938); ref. 5, p. 1013; P. R. Fontana, Phys. Rev. 125, 1597 (1962); T. Y. Chang, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI- (to be published). The author would like to acknowledge interesting conversations with Hojing Kim and Tai Yup Chang concerning these problems.

14. Here we assume that the $1/R$ expansion exists for values of R of interest in a given problem. For some values of R , in specific problems, the $1/R$ -expansion may converge very slowly, asymptotically or not at all (see for example refs. 13, 1(b) and A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. A69, 57 (1956).
15. To derive Eq. (2-18) we use the fact that $\langle \psi_K^{(0)} | H_{0,0} | \psi_3(K) \rangle = 0$ for all K (see refs. 1(a) and 9).
16. Expressions for the $C_m(K)$ and the $W_{0,m}(K)$ for $m \geq 4$ are easily obtained, see for example refs. 1(a) and 9. Furthermore many terms in the $W_{0,m}(K)$ are trivially zero, namely those involving the $H_{0,m}$ given by Eq. (2-5) and $\psi_1(K) = \psi_2(K) = 0$.
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19. Another possible general form for the zero-th order wave functions is
- $$\psi_K^{(0)} = \sum_{M_{L'_a}, M_{L'_b}} \sum_{M_{S'_a}, M_{S'_b}} \langle \varphi_a(A') \varphi_b(B') | \psi_K^{(0)} \rangle \times \varphi_a(A') \varphi_b(B').$$

Also in some problems the form

$$\psi_K^{(0)} = \sum_{M_{J'_a}, M_{J'_b}} \langle \varphi_a(R', J', M_{J'}) \varphi_b(R', J', M_{J'}) | \psi_K^{(0)} \rangle \varphi_a(R', J', M_{J'}) \varphi_b(R', J', M_{J'})$$

can be used (see for example Sec. 4). The general results

derived in this paper are valid for any of these choices of the zero-th order wave function and the actual form used will depend on the problem being considered. Since the charge distributions of the interacting atoms do not overlap, $\psi_K^{(0)}$ does not have to be antisymmetric with respect to electron interchange between a and b (see ref. 12).

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21. As mentioned in the introduction the non-relativistic energies $E(K', L', S')$ are independent of the quantum numbers M'_L and M'_S . The atomic wave functions corresponding to the same non-relativistic energy usually have the same parity and since J_1^m and O_1^m are polar vector operators the integrals $I_1(a)$ and $I_3(a)$ vanish from parity considerations. However, for example, the non-relativistic energies for the hydrogen atom are independent of the quantum numbers $L=l$ and $S=1/2$ and the wave functions corresponding to the same energy can be of different parity. Hence to prove Eqs. (3-8) and theorem I in general one must use the commutation rules given in the Appendix.
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30. This is equivalent to the dipole approximation, see for example refs. 1(b) and 3.
31. Here we use the symbol $\sum_{\Omega}^{(2S+1)}$ where S is the total spin of the diatomic molecule a-b and Ω is the projection of the total spin along the interatomic axis.
32. The value of the coefficient C_6 is taken from L. Pauling and J. Y. Beach, Phys. Rev. 47, 686 (1935); J. O. Hirschfelder and P. O. Lowdin, Molecular Phys. 2, 229 (1959).

33. The coefficient $W_{LL,4}$ is easily estimated by the procedure discussed in ref. 1(a). The interaction energy $\alpha^2 W_{LL,4} / R^4$ is negligible compared to the London dispersion energy (see ref. 1(a)).
34. For example for the relativistic interaction energy $\alpha^2 W_{LL,4} / R^4$ to be 10 per cent of the absolute value of the London energy would require $R \sim 180 a_0$ (for the H-H interaction).
35. See the discussion in ref. 1(b). These effects may be of particular interest in the scattering of beams of polarized atoms.